Photoluminescence studies and read/write process of a strong two-photon absorbing chromophore

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The optical properties of a fluorene-based chromophore exhibiting a high two-photon absorption cross section have been investigated both in the pure state and as a guest–host system in poly (*N*-vinylcarbazole). Upon irradiation with a helium cadmium (He–Cd) laser at 325 nm, the guest–host sample exhibits a blueshift with a maximum emission at 459 nm. Information written onto the samples in the blue can also be read using an Ar^+ laser. The chromophore undergoes a chemical change upon irradiation in air, and has been found to no longer exhibit upconversion after this transformation. Infrared analysis of the sample (the chromophore) before and after irradiation was carried out, and the spectra suggest the formation of a new conjugated species. Other applications we have developed using this phenomenon include the successful writing of optical device structures in polymer films where the AF-50 is a guest material. © *2000 American Institute of Physics.* [S0003-6951(00)04729-X]

Over the past two decades organic materials have shown an increasingly important potential for application in the fields of lasers and electro-optics. By exploiting the high flexibility of synthetic routes of organic systems, as opposed to conventional mineral compounds, a wide variety of organic materials can be addressed. Thin films of polymers can be very easily prepared by either spin-coating or by dip-coating polymer solutions. There are a great number of widely diversified applications of two-photon technology such as optical memory devices,[1] lithography,[2] and imaging.[3] In order to increase the density under diffraction limited optics, the digital versatile disk (DVD) system uses a laser with a shorter wavelength and a lens with a larger numerical aperture. The increase of the density from a compact disk (CD) to a DVD is by a factor of 7.3, resulting in a capacity large enough to contain a 2 h movie in its 12 cm diameter. Nevertheless, for accommodating the demands for the terabit data storage in the forthcoming information era, a breakthrough is needed either in the method of data storage or new materials, which will facilitate the storage of data with more capacity than a current DVD or CD. Currently both writing and reading are carried in the red region of the spectrum. With a layer that can be easily processed and deposited on the DVD or CD as an active layer and which can be written on in the blue region, the memory space that the device can offer triples. The driving forces behind developing two-photon based memory systems include the low cost and ease of fabrication and high data storage densities. The use of two-photon processes for optical data storage was introduced by Rentzepis[4,5] and later by Webb.[3] Recently Prasad and co-workers[6] have demonstrated the use of two-photon materials for data storage in the red region using a high two-photon absorption cross-section chromophore. Organic materials are also excellent candidates for electroluminescent (EL) devices as they can be designed to have large area light emitting displays, which can be operated at low drive voltages. The generation of light in these systems is by recombination of holes and electrons injected from the electrodes. In this letter we discuss the initial investigation of the use of a new chromophore and a polymer doped with this chromophore as a memory storage device by conducting photoluminescence (PL) studies and the read/write process in the blue region.

The commercially available polymer poly(*N*-vinylcarbazole) (PVK) (Aldrich Chemicals, USA) was doped with a chromophore with high two-photon absorption cross section. PVK is an extensively studied polymer in regard to its

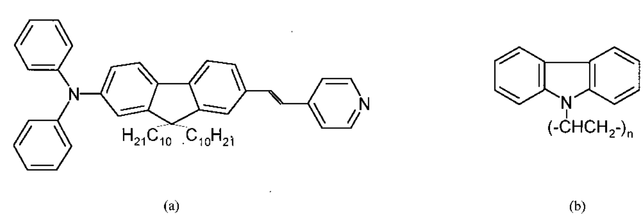

FIG. 1. (a) Molecular structure of AF-50 and (b) molecular structure of PVK.

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[c]We sadly report the death of our good friend and colleague Bruce A. Reinhardt and humbly dedicate this work to his memory.

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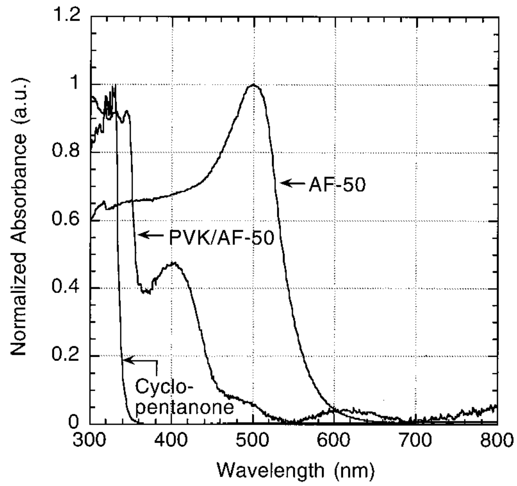

FIG. 2. Optical absorption spectra of AF-50, PVK-AF-50 (mixture), and the solvent (cyclopentanone).

EL properties.[7] The basic concept is to employ a polymer doped with a chromophore for use in memory storage devices. The new chromophore (N,N-Diphenyl-7-{2-(4-pyridinyl)-ethenyl}-9,9-di-n-decyl-9H-fluorene-2-amine) AF-50,[8] shows excellent solubility in a variety of common solvents and was used for the PL studies. Figure 1 shows the molecular structures of the materials used in this study. AF-50 exhibits a very high two-photon absorption cross section[9,10] making it an ideal candidate for memory devices and photo-

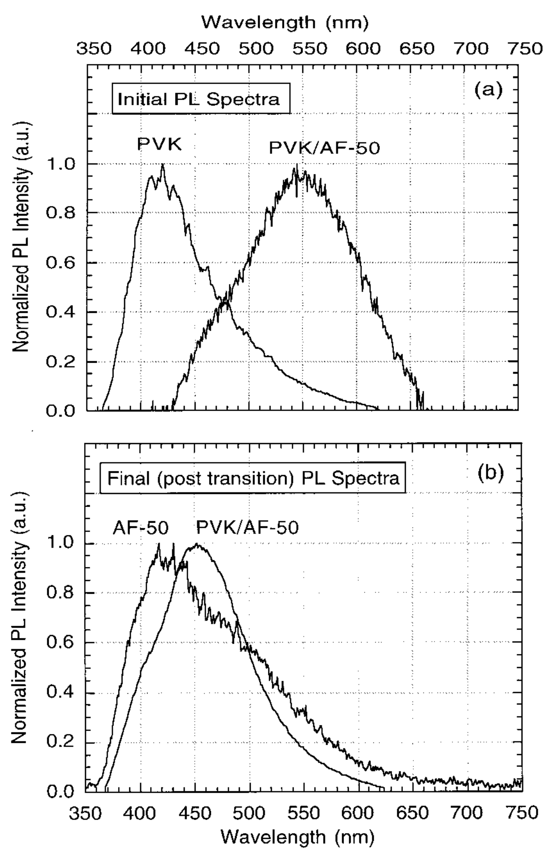

FIG. 3. Photoluminescence spectra of the chromophore and the polymer doped with the chromophore before (a) and after (b) irradiation with the He–Cd laser at 325 nm.

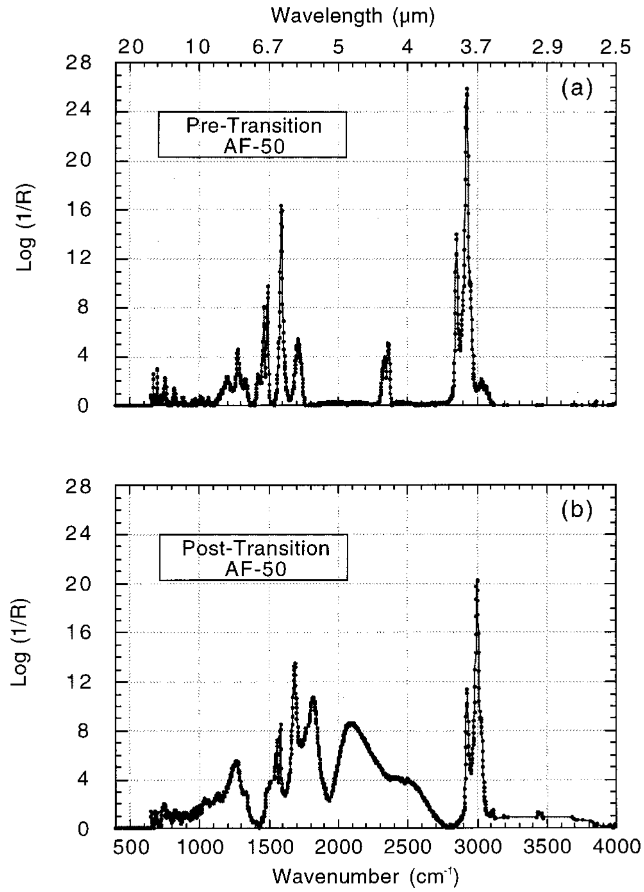

FIG. 4. (a) IR spectra of the chromophore AF-50 before irradiation with the laser and (b) IR spectra after irradiation, showing the chemical change in the chromophore.

diode emission. We have demonstrated here an application of the chromophore in read/write applications.

The solutions of poly(vinylcarbazole) (PVK)-AF-50 (4% by weight in PVK) and AF-50 (4% by weight in the solvent) were prepared by dissolving the samples in cyclopentanone and stirring them overnight at 60 °C at 750 rpm. The solutions were filtered using a 0.2 μm Whatman filter and then spin coated onto base cleaned glass slides and dried in the oven at 65 °C for 2 h for the solvent to evaporate. The films (AF-50 on Si substrates) had a thickness of 2500$\pm$75 Å and a refractive index of 1.68 (at 630 nm) as determined by using a spectroscopic ellipsometer (VASE®, manufactured by J. A. Woollam & Co, U.S.A.). Electronic absorption spectra were obtained using a Perkin-Elmer UV/VIS/NIR spectrometer and the absorption spectra for the both PVK-AF50 mixture and AF-50 in cyclopentanone are shown in Fig. 2. AF-50 in cyclopentanone was found to have a λ_{max} of 500 nm.

The photoluminescence studies were carried out using a cw He–Cd laser and information was ''written'' onto the sample using the 325 nm line of the laser. The emission was collected by a Nikon microscope with a 10$\times$ objective and fed to a 0.5 m monochromator (ARC SpectraPro 500) using a near ultraviolet to visible grade optical fiber. The optical power used to write the information onto the sample was set at 8 mW. PL spectra taken immediately after laser incidence, seen in Fig. 3(a), show a marked difference between the

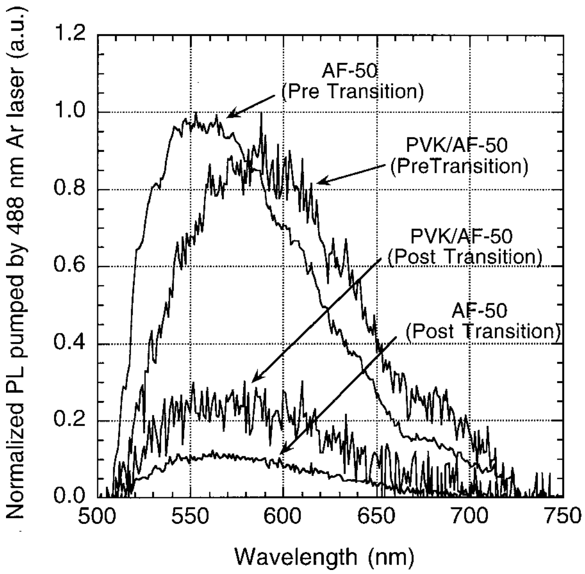

FIG. 5. Normalized photoluminescence spectra of the samples obtained using an Ar^+ laser (488 nm). Data show the ''readback'' of the information ''written'' onto the samples using the He–Cd laser (325 nm). The samples after irradiation by the He–Cd laser do not show any emission when exposed to the Ar^+ laser, unlike the pretransition samples.

emission from the pure AF-50 sample (broad emission in the blue, with a peak at 450 nm) and the dilute AF-50 solution in PVK (broad emission in the green/yellow with a peak at 546 nm). Laser irradiation for 5–10 s causes a blueshift in the PL spectrum from the PVK/AF-50 sample [shown in Fig. 3(b)] bringing it close to the corresponding PL spectrum of the AF-50 sample. No further changes in the PL spectrum were observed with continuing laser irradiation. The PVK/AF-50 appears to undergo a chemical change upon laser irradiation causing the blueshift in the PL spectrum. The IR data for the pure AF-50 suggests the formation of a new conjugated system, such as a ketene imine, as evidenced by the new broad absorption at $\sim$2000 cm^{-1} (Fig. 4). Attempts to isolate the transformed species and characterize it in further detail are in progress. It can be seen in Figs. 4(a) and 4(b) that many of the main IR bands are unaffected by this reaction. This chemical change has been noticed by us to be an irreversible one. The addition of PVK to the sample seems to slow down the process of the shifting of the PL curve into the blue region compared to the rapid change observed with pure AF-50. Samples of the host polymer (PVK) do not show a shift in the photoluminescence spectra when irradiated with the He–Cd laser. This chemical change in the sample facilitates readback of the information written onto the sample. Readback was carried out using an Ar^+ laser (488 nm at 20 mW). Figure 5 shows the normalized PL data for the samples before and after irradiation with the He–Cd laser. Other applications we have developed using this phenomenon include the successful writing of optical device structures in polymer films where the AF-50 is a guest material.[11] In particular Mach–Zehnder interferometers have been optically written into this organic system and successful waveguiding achieved in these devices.

As mentioned earlier in this letter, AF-50 exhibits very efficient frequency-upconverted fluorescence, which is an important property of the material being used for memory storage. This effect was observed here only in the region that had previously not been irradiated with the 325 nm laser (writing of information on the sample). Analysis of this change in the property of the sample and exploration of the possible application of this behavior in such films is in progress.

In conclusion, we have been able to write information optically onto a guest–host system (a polymer doped with an efficient two-photon up-converting chromophore) and then carry out the ''read back'' of the information. The fabrication of EL devices using this organic guest–host system is in progress.

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